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THESIS
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THE RELATION OF AMMONIUM SULFATE TO ACIDITY AND TOXICITY OF SOILS.

Foreword.

It has been observed for many years that ammonium sulfate has in time produced an infertile condition in a soil to which it is applied year after year. This thesis demonstrates (a) that this salt forms soluble sulfates by an exchange with the bases existing in the soil and (b) that these are freely removed in the drainage water.

In the presence of much calcium carbonate, the formation of calcium sulfate occurs more prominently than any other salt. *In its absence*, the sulfates of iron, aluminium and manganese are formed, resulting in a marked change in the absorptive properties of the soil. These salts upon hydrolysis give a positively acid reaction and cultures in them of different kinds of seedlings showed them to be toxic in relatively low concentration.

Introduction.

The subject of acid soils and the nature of the acidity is rather prominently before ~~the~~ agricultural investigators at the present time.Much has been written and many theories have been advanced as to the nature of the acid or acids present in the so called acid soils,but none of the theories have met with general acceptance.While this paper does not aim to present a new theory,it does aim to show,that the long continued use of sulfate of ammonia without lime,does not produce an acid soil,if we define an acid soil as one containing a free acid.

Acid soils in general may be divided into two groups, namely:those whose acidity is due to what might be called natural causes,as the peat and bog soils,and secondly, those whose acidity is the result of chemical fertilizers, as the ammonium sulfate fertilized soils.Most of the early work,especially of the European investigators was done on the first group of soils,which I believe accounts for the prominence attained by the humic acid theory.

At present the two most important theories in regard to soil acidity are the colloid theory and the free acid theory.

The free acid theory might be said to have originated with the investigations of Sprengel[1] in 1826 when he discovered the humic acids and their salts.A few years later Berzelius[2] (1839) added cren and apocren acids,the latter being an oxidation product of the former.Later Mulder(1840) Herman,Sestini,Truh,Eggertz,Berthelot and Andre all found humic acids of one kind or another.All of these "acids" which these investigators found were undoubtedly laboratory products and in the light of recent investigations, probably,colloidal absorption compounds.Of late years we find no investigator who claims to have separated or isolated a free acid from the soil.Some investigators claim to have obtained an acid extract from acid soils but did not identify the acid or acids;other investigators believe free acids exist in the soil because of the action of the soil with neutral salt solutions.

Among the first investigators to study the action of soil with neutral salt solutions was Way[3].Using Ammonium salt solutions he found that the basic radical of the salt

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[1] Archiv fur die Gesamte Natur lehre,1826.
[2] Lehrbuch der Chemie 3 Auflage,p 389.
[3] Jour.Roy.Agr.Soc.Vol.11 (1850) & Vol.13 (1853)

was absorbed while the acid radical remained in solution, as the calcium salt, the quantity of lime removed being equivalent to the amount of ammonia absorbed. Voelcker[1] continued the work of May and confirmed his results. Beyer[2] in studying the absorption, found that it depended on the amount of iron and aluminum oxides present in the soil. Morse and Curry[3] in working on clay, with potassium and sodium salts, found that the bases were absorbed and that in exchange, calcium, magnesium, iron and aluminum were removed. The amount of iron and aluminum were equivalent to the acid content of these solutions. Other investigators[4] in studying the action of salt solutions on soils, have in general arrived at similar conclusions, namely, that the action consists of an exchange of base between silicates in the soil and the salt solution. Some[5] have claimed that the exchange was quantitative and thus was due to a chemical reaction, while others[6] have believed it due to the replacement of the bases in the soil colloids by the more strongly absorbed base of the salt solution. More recently, Parker[7] stated that the dissolved bases were due to a secondary reaction of the acid set free when the base was absorbed.

The acid extracts obtained by those investigators who believe that more base is absorbed than is removed from the soil can, I believe in most cases be explained by the presenge of iron and aluminum salts as has been shown by Veitch[8], Morse and Curry[9], and as was found by Harris[12], tho he does not consider them as responsible for the acidity. As to the effect of ammonium sulfate on soils the following investigators may be cited.

While May and Voelcker were among the first to note the effect of ammonium sulfate on soils they studied the laboratory phase of the question rather than the effects in the field. Lawes and Gilbert[13] at Rothamstead were probably the first to note a difference between the plots fertilized with ammonium sulfate and sodium nitrate.

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1. Jour. Roy. Agr. Soc. Vols. 21, 60, 62.
2. An der Landwirtschaft Bd. 1 & 2.
3. Rpt. N. H. Agr. Expt. Sta. 1906-1908 p 274.
4. Armsby Amer. Jour. Science Vol. 14 (1877) p75.
   Van-Bemmelen Landw. Versuch, Stationen, Vols. 21 & 35.
   Baumon & Gully, Mitteil der Kgl. Bayr. Moorkultureanstalt 1909, No. 3.
   Kozai-Chem Zeit Vol. 32 p 1187.
   Thaer - Jour fur Landw. 59 (1911)
   Prianischikow - Landw Versuch Stationen Vol. 79-80 (1913)
5. May loc. cit.
   Voelcker loc. cit.
   Peters Landw. Vers. Star. 2 (1860)

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In studying the drainage waters from the differently fertilized plots, they found that the plots treated with ammonium sulfate had much larger amounts of calcium removed than the other plots. They reached the conclusion that all of the sulfuric acid from the ammonium sulfate was removed as calcium sulfate.

Wheeler[1] found that the long continued use of ammonium sulfate without lime caused the soil to become acid, and that an application of lime corrected this acidity. Hall and Miller[2] found that the loss of calcium carbonate was increased when ammonium salts were used by an amount equivalent to the acid of the fertilizer. Nitrate of soda diminished this loss of calcium. Hall and Gimingham[3] state that the constituents of the soil do not react with solutions of ammonium sulfate to produce a free acid. The free acid is of biological origin. In a later publication Hall[4] concluded that the acidity produced by the long continued use of sulfate of ammonia is caused by certain micro-fungi in the soil which split up the ammonium sulfate in order to obtain the ammonia and thereby set free sulfuric acid. Infertility of such soils results because the regular bacterial changes in the soil are suspended by the acidity, and instead fungi permeat the soil and seize upon the manure. The remedy is to add lime to keep the soil neutral. Hunt[5] also found that the long continued use of sulfate of ammonia brought the soils into an acid condition which was especially harmful to corn and clover. Voelcker[6] (1914) states that at Rothamstead, on plots where ammonium sulfate has been applied alone and in combination with mineral manures the soil was so acid that crops could not be produced. Brown[7] states that when ammonium sulfate is applied to soil it leads to a developement of acid conditions because of the production of sulfuric acid. If sufficient lime is present the acid unites with it.

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6. Van Bemmelen - see above.
   Bauman & Gully - see above.
7. Jour. Agr. Research Vol.1 No.3(1913)
8. Veitch - Jour. Amer. Chem. Soc. 26(1904)
9. Loc. cit.
12. Mich. Tech. Bul. 19(1914)
13. Rothamstead Memoirs, Vol.5 p 97.

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[1] Ann. Rept. R. I. Expt. Sta. 1893, 1895-6.

[2] Proc. Roy. Soc., Ser, B77(1905) p 1-32.

[3] Jour. Chem. Soc. Vol. 91(1907) No. 534.

[4] Jour. Roy. Agr. Soc. 70(1909) p 12.

[5] Penn Exp. Sta. Bul. 90.

[6] Jour. Roy. Agr. Soc. 1914.

[7] Iowa Expt. Sta. Bul. 151 (1914)

White[1] in a recent publication states that the differences in amount of acidity of the ammonium sulfate treated plots in Pennsylvania is due to the accumulation of humic acids. This conclusion is arrived at because of the large amounts of "free" humus found on the ammonium sulfate treated soils.

The soil used for the various experiments described in this paper was taken from one of the oldest fields on the Station farm. A record of this field has been kept for thirty-three consecutive years, and in that time only chemical fertilizers have been applied. Since 1890, when the present fertilizing scheme was inaugurated, the field has been used to compare different forms of nitrogen fertilizers. The plots are 1/10 acre in area and are divided by a two-foot path. In addition each plot has been divided into two equal parts, one of which has been limed. Through the center of each plot there is a two-inch tile drain at an average depth of three feet.

The chemicals applied annually, since 1890, to the plots studied have been as follows:

Plot 0. Manure, dissolved boneblack, sulfates of potash and magnesia.
Plot 1. Nitrate of soda, dissolved boneblack, muriate of potash.
Plot 5. Sulfate of ammonia, dissolved boneblack, sulfates of potash and magnesia.
Plot 6. Sulfate of ammonia, dissolved boneblack, muriate of potash.
Plot 7. No nitrogen, dissolved boneblack, muriate of potash.
Plot 8. Sulfate of ammonia, dissolved boneblack, muriate of potash.

The amounts applied have been 45 pounds of nitrogen per acre in nitrate of soda, sulfate of ammonia or manure, 80 pounds of phosphoric acid per acre in dissolved boneblack, and 125 pounds of potash per acre in muriate of potash or double sulfates of potash and magnesia. On plot 0 the phosphoric acid and potash naturally present in the manure have been supplemented by enough chemicals to make 80 pounds of phosphoric acid and 125 pounds of potash. The only organic matter added has been in the form of crop residues and catch crops plowed under. Since the present schemem of fertilization was inaugurated, the field has been limed as follows: in 1898 and 1905 at the rate of one ton per acre and in 1909 and 1913 one-half of each plot at the rate of two tons per acre.

The first soil samples were taken from these plots in 1912, just before the fertilizers were applied and after the land had been plowed. The second set of samples was

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[1] Ann. Rept. Penn. Agr. Exp. Sta. (1912-1913).

taken in the spring of 1913,immediately after the lime had been applied and harrowed in,but before the application of any fertilizers.Subsequent samples were taken in the spring of 1914 and in the fall of 1915.The soils were taken to the laboratory as soon as sampled,thoroughly mixed and air-dried.In subsampling,the soil was passed through a sieve having seven holes to the linear inch.No finer sieve was used,as it was desired to have the soil in as nearly actual field condition as possible.

The crops grown in the years previous to the sampling (1911 and 1912) were corn with clover sown in the corn during the fall.The crops were the same both years,as the clover made a poor catch in 1911 and was plowed under.In 1913 millet was grown as the clover planted the previous fall again failed to live through the winter.The millet made a good growth on all of the plots,the limed ends of the two sulfate of ammonia plots 6 and 8 having the best stand in the field.Of the unlimed plots the two sulfate plots were about equal to any of the others tho not as good as the limed ends.As millet is a crop adapted to "sour" soils[1] the above results are what might be expected.

The millet was cut in September and the ground left bare during the winter.Fall planting of clover and grass having proved a failure,spring planting was tried in 1914. The plots were accordingly seeded with a red clover and grass mixture together with oats as a nurse crop.The oats were cut in July and showed marked differences both between the limed and unlimed ,and between the different fertilizer treatments.The no nitrogen,with plot 6 were the poorest in the field,while the nitrates were the best. The differences between lime and no lime were not noticeable to any extent on the nitrate plots,but were quite marked on the sulfate of ammonia and no nitrogen plots. The differences however seemed to be largely in quantity. The germination on the no nitrogen and sulfate of ammonia plots were seemingly poorer than on the other plots.

After the removal of the oats the clover made a good growth,that on the limed half of the no nitrogen plots being the first to show above the stubble.The clover on the whole area of the nitrate plots and on the limed halves of the ammonia plots 5,6,&8 followed about one week later. The clover on the no nitrogen plots continued to lead all the other plots in size and vigor of growth and began to bloom several days ahead of them.The nitrate of soda plots showed practically no difference between the limed and unlimed areas,but was not quite as good as the limed,no nitrogen areas. The limed areas of the sulfate of ammonia were similar to the nitrate of soda plots.The unlimed areas of all the other plots except the nitrate of soda plots produced a

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1.Wheeler,J.[illegible].D.A.Farmers Bul.77,1915.

slower growing crop but the stand was practically as heavy.The clover on the unlimed areas of the sulfate of ammonia plots showed the greatest differences from the limed areas as well as the other unlimed areas.The plants were inferior in every way,having a stunted appearance.The clover was not cut as it was considered best to leave the tops as a covering for the roots during the winter.In the following spring of 1915 the clover came up well on all of the plots with the exception of the unlimed areas of plots 5,6 &8,where the growth was poor but a fair stand of grass came up.This difference between the unlimed area of these plots and the other plots of the field both limed and unlimed increased as the season advanced,and at the time of cutting there was more grass than clover on these plots,being only a foot tall when cut.The clover on the other plots made as good a growth as in the previous fall. The grass however did not grow to a great height.

PART I. ABSORPTION STUDIES.

The first part of the investigation was carried on with different strenghs of ammonium sulfate solutions to determine,first if there was a difference in the amount of ammonia absorbed by the differently treated plots and secondly,whether the resulting solutions gave an acid reaction and thirdly,what solvent action if any the ammonium sulfate had on the different soil constituents.

The concentrations of ammonium sulfate used most were one-tenth normal(N/10)),normal(N) two and one half normal ($2\frac{1}{2}$N) and five times normal(5N).

Unless otherwise stated the soil was treated as follows: 150 grams of air-dried soil were treated with 750 cubic centimeters of the ammonium sulfate solution.The mixture was allowed to stand,with frequent shakings,for two hours, and then filtered through an unwashed filter paper.In every case the filtrate was perfectly clear but yellow,the intensity of the color varying between the limed and the unlimed soils and with the strength of the solution used.

The solutions were analyzed for the amount of ammonia absorbed,and for the iron and aluminium,calcium,sodium, potassium,sulfates,chorides and nitrates removed.

All of the extracts when tested for their reaction, using litmus and phenolphalein were found to be neutral, thus proving that the ammonium sulfate had not produced any free acid.

Absorption of Ammonia.

The amount of ammonia absorbed was determined by the amount removed from the solution of ammonium sulfate. The ammonia was determined by the magnesium oxide method.

From 1 to 10 cc of the solution was used for a determination, depending on the concentration of the solution.

Table II gives the amount of the ammonia absorbed by 100 grams of air-dried soil.

Table II.-Milligrams of Ammonia absorbed from Ammonium-sulfate Solutions by 100 Grams of Air-dried Soil.

Plot.	N/10 Solution	N Sol.	2½N Sol.
Plot 0 Limed	72.5	212.5	-
Plot 0 Unlimed	60.0	162.5	175
Plot 1 Limed	72.5	162.5	250
Plot 1 Unlimed	60.0	200.0	275
Plot 6 Limed	77.5	187.5	175
Plot 6 Unlimed	42.5	62.5	100
Plot 7 Limed	62.5	200.0	100
Plot 7 Unlimed	57.5	125.0	225
Plot 8 Limed	67.5	150.0	150
Plot 8 Unlimed	42.5	87.5	235

Taking the plots as a whole we find that with an increase in the concentration of the ammonium-sulfate solution used the amount of absorbed ammonia increases. Comparing the amounts of ammonia absorbed by the soil from the different plots we find that the unlimed ends of plots 6 and 8 consistently show a smaller absorption than any of the others, except in one case with the strongest solution by soil from plot 8. The variations in amounts absorbed on the remaining plots are within the limits of possible error, on account of the concentration of the solutions employed.

The results show that some change has been brought about in the plots receiving the ammonium sulfate without the addition of lime. If we assume that the absorption is due to colloids it would seem that the amount of colloids present in the ammonium sulfate plots had been decreased. That the absorption is a physical phenomenon rather than a chemical one is further borne out by the amount of dye absorbed by these different soils.

Absorption of Dyes.

The dyes used were aniline blue, aniline green, corraline and eosine. The method of procedure was as follows: 10 grams of soil were shaken up with 100 cubic centimeters of the dye

and then set aside until the supernatant liquid was clear. Fifty cubic centimeters were then pipetted off and compared with a standard dye solution in a colorimeter.

The eosine and corraline were not absorbed by the soil in a measurable quantity,if at all.One hundred cubic centimeters of the aniline blue and aniline green in concentrations below 50 parts per million were entirely decolorized by 10 grams of soil.The concentrations used were 50 and 100 parts per million.

Table III.-Dye Absorbed by 10 Grams of Soil from 100 Cubic Centimeters of Dye Solution.

Plot.	AnilineBlue (50 Parts per million)	Aniline Blue (100 Parts per million)	Aniline Green (100 Parts per million)
Plot 0 Limed	49.68	98.45	97.00
Plot 0 Unlimed	49.71	98.50	95.00
Plot 1 Limed	-	99.12	96.67
Plot 1 Unlimed	49.76	98.94	95.97
Plot 6 Limed	49.73	98.58	95.30
Plot 6 Unlimed	49.33	93.54	87.50
Plot 7 Limed	49.74	98.40	96.00
Plot 7 Unlimed	49.69	98.24	94.75
Plot 8 Limed	49.73	98.61	94.50
Plot 8 Unlimed	-	97.76	92.00

Here we see the same differences as were found in the preceeding table of the ammonia absorbed,tho the differences are not so great.There is an increase in the dye absorbed with an increase in the concentration used and a less absorption by the soilfrom the unlimed areas of plots 6 and 8,the two sulfate of ammonia plots.The limed ends of the plots also show a slightly higher absorption than the unlimed.

The dyes seem to have a deflocculating effect on the clay in the soil,as they settle much more slowly than with a corresponding water treatment.This is particularly noticeable on the limed end of the plot,from which the solution,even at the end of twenty-four hours,was too turbid to be used in a colorimeter.

Calcium Oxide Removed.

The amount of calcium removed from the soils by the different treatments was determined by the titration method with potassium permanganate.The amounts removed from 100 grams of air-dried soil are shown in Table IV.

Table IV.-Milligrams of Calcium Oxide removed from 100 Grams Air-dried Soil by Distilled Water and by Different Solutions of Ammonium Sulfate.

Plots	1912.				1913.			
	Water	N Solution	2½ N Solution	5 N Solution	Water	N/10 Solution	N Solution	2½N Solution
Plot 0 Limed	-	-	-	-	12.26	103.75	218.05	237.30
Plot 0 Unlimed	-	-	-	-	7.04	61.98	108.45	116.55
Plot 1 Limed	69.45	176.05	182.65	171.00	10.95	95.65	205.15	242.85
Plot 1 Unlimed	6.66	106.95	117.80	124.60	6.91	61.30	116.65	120.60
Plot 6 Limed	12.73	116.75	118.05	150.50	11.21	82.19	156.65	184.90
Plot 6 Unlimed	8.42	36.47	42.08	53.90	7.82	18.19	27.11	25.26
Plot 7 Limed	10.17	177.05	178.70	175.50	10.43	99.03	205.17	243.87
Plot 7 Unlimed	8.42	78.20	83.90	77.50	6.78	43.12	70.25	71.41
Plot 8 Limed	11.92	122.05	131.10	106.50	9.91	92.95	199.05	233.66
Plot 8 Unlimed	8.77	58.20	59.60	65.85	8.21	37.05	60.10	60.63

Considering the table as a whole we find that more calcium is removed from the limed ends than from the unlimed.The effect of the application of lime in 1913 is plainly shown by the increased amount of calcium removed from the limed ends in 1913 over 1912 by the normal 2½ normal solutions.Further,in 1912 no increase is noted in the amount of calcium removed from the limed plots with an increase in the concentration of ammonium-sulfate solution used.In 1913,however,an increase is noticed with each increase in the concentration of the ammonium-sulfate solution. With the unlimed ends of the plots no such increase is noticed either year,except between the one-tenth normal and normal concentrations.

Studying the variations between the different plots we find the chief difference to be the smaller amount of calcium removed from the two sulfate plots 6 and 8,both limed and unlimed.ends.

This indicates that the previous fetilization with ammonium-sulfate has depleted these soils of this element.That it has a solubility effect on the calcium in the soil is borne out by the larger amount of calcium removed in the water extracts from the two sulfate plots.That sodium nitrate has had a protective action on the calcium is shown by the larger amounts of calcium removed from the nitrate plot than from the no nitrogen plot,seven.The presence of the soda has prevented the soil from becoming poor in calcium.When larger quantities of lime are present the protective action of the sodium is not so evideht

Sodium and Potassium Removed.

Owing to the large mass of ammonium sulfate and the small amount of sodium and potassium in solution it was difficult to make exact determinations of these elements. Several methods were studied,but the method of weighing the sodium and potassium as the double chlorides,and then deter-

mining the potassium as the chlorplatinate was finally adopted.The results obtained are as accurate as could be expected under the circumstances.

Table V. -Milligrams of Sodium Oxide removed from 100 Grams of Air-dried Soil by Different Solutions of Ammonium Sulfate.

Plot	N/10 Solution	N Solution	2½ N Solution
Plot 0 Limed	13.25	32.60	-
Plot 0 Unlimed	11.40	20.40	25.45
Plot 1 Limed	14.05	-	23.05
Plot 1 Unlimed	13.50	20.40	22.55
Plot 6 Limed	7.95	17.75	21.20
Plot 6 Unlimed	9.80	-	18.85
Plot 7 Limed	9.55	19.90	22.00
Plot 7 Unlimed	10.10	18.30	24.40
Plot 8 Limed	8.75	19.90	22.00
Plot 8 Unlimed	8.20	-	18.75

Milligrams of Potassium Oxide removed from 100 Grams Air-dried Soil.

Plot 0 Limed	12.00	13.60	-
Plot 0 Unlimed	10.75	27.15	20.85
Plot 1 Limed	14.45	-	27.15
Plot 1 Unlimed	10.75	23.70	23.05
Plot 6 Limed	10.00	21.50	24.95
Plot 6 Unlimed	12.65	-	21.50
Plot 7 Limed	17.70	31.25	28.75
Plot 7 Unlimed	13.90	26.85	29.05
Plot 8 Limed	14.55	26.20	25.25
Plot 8 Unlimed	11.70	-	22.75

As with the calcium the sodium and potassium removed increase with the concetration of the ammonium sulfate solutions.Unlike the calcium there are no marked differences in the amounts removed from the limed and unlimed ends of the plots,or from the different plots. This would seem to indicate that the continued use of ammonium sulfate has not diminished the amount of sodium and potassium in the soils,or,stated differently,the absence of lime has not increased the rate at which they were removed from the soils.

Iron and Aluminum Removed.

Iron determinations could be made colorimetric only after the largest part of the ammonium sulfate had been removed,as ~~the~~ it prevented the developement of the color with the thiocyanate.No colorimetric determinations were made on the 2½ and 5 normal extracts as the amonnt of ammonium sulfate was too large to be driven off by ignition without some mechanical loss.

In the 2½ normal and 5 normal concentrations of ammonium sulfate extracts,iron and aluminum were determined together by precipitating with ammonia as the hydrate,The precipitates were all light in color showing that they were mostly aluminum,but all had some iron present.

No iron was found in any of the water extracts or in the extracts from the limed ends of the plots with any of the ammonium sulfate solutions,except on plot 6 with 2½ normal solution,and on all the plots with the 5 normal solution.In all the extracts from the unlimed ends of the plots iron was found in varying amounts.

Table VI.-Milligrams of Iron Oxide removed from 100 Grams of Air-dried Soil by Different Solutions of Ammonium Sulfate.

Plot	N/10 Solution	N Solution.
Plot 1 Unlimed	.40	.79
Plot 6 Unlimed	.46	.51
Plot 7 Unlimed	.43	.50
Plot 8 Unlimed	.89	1.02

Table VII.-Milligrams of Iron and Aluminum Oxides removed from 100 Grams of Air-dried Soil by Different Solutions of Ammonium Sulfate.

Plot	2½ N Solution	5 N Solution
Plot 1 Unlimed	4.25	6.50
Plot 6 Unlimed	12.00	33.00
Plot 7 Unlimed	8.00	7.50
Plot 8 Unlimed	7.75	28.00
Ploe 6 Limed	2.50	8.00

The most striking difference is in the amount of iron and aluminum oxide removed from the two sulfate plots 6 and 8, with the higher concentration. In comparison with the amounts of iron removed by the N/10 and N solutions, the large increase in the amounts of combined oxides removed by the higher concentrations would seem to be due to aluminum oxide.

Acids removed.

In determining the acids in the ammonium sulfate solutions, the large amounts of ammonium sulfate presented difficulties which interfered with the accuracy of the determinations in every instance.

Sulfuric Acid Removed.

In determining the sulfates the small aliquot which had to betaken owing to the amount of sulfates present made a slight error in weighing, assume large proportions when figured to sulfates removed from 100 grams of soil. This was especially true of the 2½ normal and 5 normal extracts. In almost every case, however, more sulfates were found in the extracts than were present in the original solutions used. Where this was not the case the difference between the amonnt present in the original solution and the amount found in the extract was so small as to easily come within the limit of error. The results indicated that there was no accumulation of sulfuric acid in the soil which would cause it to become acid, as has been claimed by some investigators.

Hydrochloric Acid Removed.

In trying to determine the amonnts of hydrochloric acid in the extract by titration it was found that the ammonium sulfate prevented the development of the color. In making gravimetric determinations no precipitate or cloudiness was observed using 100 cubic centimeters aliquots. This shows that the chlorides if present at all were present in concentrations of less than one part per million of extract, or less than one-tenth of a milligram removed from 100 grams of soil.

Nitric Acid Removed.

Nitric acid could not be determined with any degree of accuracy by the colorimetric method. The few determinations made on the more dilute extracts indicated that there was no appreciable difference in amount removed between the different plots. The average amount found was 1.5 parts per hundred thousand.

Calcium Absorption.

The absorption of calcium by the soil was studied in connection with the determination of soil acidity by the Veitch method. This method is essentially a measure of the absorption of lime by the soil and not a measure of any free acid.

The Veitch method was used on soil from the unlimed and limed ends of plot 6. No difference in the amount of absorbed calcium was noted between the limed and unlimed areas, both having absorbed at the rate of 2,545 pounds of calcium oxide per acre (2,000,000 pounds of soil per acre).

A second method, using the same substance, was also tried. In this method 100 grams of air-dried soil were shaken with 500 cubic centimeters of a saturated calcium-hydrate solution and filtered after two hours. An aliquot of the filtrate was then titrated and the amount of absorbed lime determined. This method gave a much higher absorption than was found by the Veitch method. No difference in the amount of calcium absorbed between the limed and the unlimed ends was observed. The calcium oxide absorbed was equal to 11,776 pounds per acre.

A third method, taking a solution of calcium sucrate, was also used. Ten grams of soil were shaken with 50 cubic centimeters of the solution, filtered after two hours and an aliquot titrated. Two strengths of the calcium-sucrate solution were used,- a saturated solution and another one-tenth as strong. The absorption of calcium was the same with both solutions and on both the limed and unlimed areas. The absorption was much greater than with either of the two previously mentioned methods. The unlimed end absorbed at the rate of 26,660 pounds of calcium oxide per acre, while the limed end absorbed at the rate of 23,850 pounds per acre. The greater absorption of the calcium from the sucrate solutions is due to the greater concetration of calcium in these solutions. The Veitch method does not measure the true absorptive capacity of the soil, but measures the absorption up to the point of alkalinity of the soil. That the soil can absorb more calcium after the point of alkalinity is reached is shown by the results obtained by the other methods. With the calcium-sucrate solution the limit of the amount of calcium which the soil can absorb seems to have been reached, as with an increase in the concentration no increase in the amount of calcium absorbed is noted.

It is of interest to compare the results obtained by the above methods with the calcium oxide equivalent obtained with the Hopkins method of determining soil acidity. With this method a marke difference between the limed and the unlimed areas of plot 6 is found. The unlimed area has a much higher calcium oxide equivalent than the limed area. The calcium oxide equivalent of the limed end is 631 pounds of calcium oxide per acre, while the unlimed gives an equivalent of 4,976 pounds per acre.

This "acidity", however, is not due to the presence of free acids, either soluble or insoluble in water, but is probably due to the presence of iron and aluminum salts. When the soils

are shaken up with the normal potassium-nitrate solution, as the method calls for an action resembling a double decomposition takes place between the iron and aluminum compounds and the potassium nitrate with the formation of the easily hydrolyzable iron and aluminum nitrateswhich go into solution. When the aliquot is titrated the titration shows the amount of nitric acid present in combination with iron and aluminium, as is evidenced by the heavy flocculent precipitate which forms during the titration. In order to determine if nitrates of iron and aluminium hydrolyze readily, known solutions of those salts were made up and titrated. It was found that the entire quantity of nitric acid present could be titrated.

Summarizing the results obtained by the different methods, we find that the soil absorbs increasing amounts of calcium from increasing concentrations of calcium solutions, and that the limed and unlimed plots absorb practically like amounts of actual calcium.

Analysis of Drainage Waters.

To determine if the composition of the drainage waters would throw any light on the effect of long-continued use of ammonium sulfate as a fertilizer, the following analyses of drainage waters from the plots studied in the first part of this bulletin were undertaken.

The drainage waters were collected in the spring and fall of 1912 and 1913. Most of the samples were collected in the spring after the frost had left the ground. Only three samples were taken in the late fall. No.drainage took place during the summer and early fall. The waters at alltimes were clear from sediment of any kind. In the spring of 1912 five sets of samples were collected, the first on March 18 and the last on May 17. In the fall a set of samples was collected on November 5 and December 6. In 1913 the first samples were taken on March 9. Five subsequent sets of samples were taken at intervals of one week. Another set was obtained on December 8.

The waters were analyzed for total solids, fixed solids, calcium, sodium, potassium, iron, chlorides and sulfates. As the nitrates vary between wide limits within short spaces of time no attempts were made to determine them, except when the water could be analyzed as soon as collected. Iron was found in traces only in any of the waters.

The amount of drainage varied considerably between the different plots. The amount can be estimated only by the apparent flow from the outlets. Plot0 had the largest amount, with plots 1 and 7 closely following in the order named.Plots 6 and 8 had the smallest amount.The differences can be explained in part by the general slope of the field.Plots 0 and 1 are the lowest in the field.While the slope is not great it is probably enough to cause some increase on the lower plots.The actual amount of drainage for the year could not be determined, as means for measuring the flow were not acailable.

Table VIII.-Average Composition of Drainage Waters in Parts per 100,000.

1912

Plot	Total Solids.		Loss on Ignition.		Calcium Oxide.		Sulfur Trioxide		Chlorine.	
	Spring	Fall	Spg.	Fall	Spg.	Fall	Spg.	Fall	Spg.	Fall.
0	--16.86	17.95	5.0	6.6	2.06	4.25	5.36	6.07	1.42	1.66
1	--24.60	27.60	7.2	7.9	2.43	4.30	8.16	7.87	3.05	4.27
6	--27.60	35.50	5.7	8.9	4.39	11.85	11.61	13.29	2.81	3.99
7	--21.30	23.40	7.0	6.9	2.49	7.20	8.72	8.17	2.15	3.58
8	--30.30	32.90	7.5	7.8	4.82	10.45	12.95	12.79	2.55	3.15

1913

Plot	Total Solids		Loss on Ignition		Calcium Oxide		Sodium & Potassium Chlorides	Sulfur Tri-oxide		Chlorine.	
	Spg.	Fall	Spg.	Fall	Spg.	Fall	Spg.	Spg.	Fall	Spg.	Fall
0	--17.9	22.6	3.78	6.4	4.05	4.51	5.0	6.92	7.67	1.26	1.45
1	--22.7	27.5	3.50	5.0	3.82	3.99	10.2	6.86	7.61	3.19	4.97
6	--24.0	33.1	5.46	6.3	6.71	8.30	4.6	8.88	11.13	2.79	4.83
7	--20.2	26.9	4.72	6.0	5.24	6.73	4.9	6.49	6.65	2.72	5.62
8	--26.4	36.8	5.28	6.5	8.03	9.67	5.2	9.79	11.70	2.88	5.35

Comparing the results plot by plot the first difference noted is in the amount of total solids removed.More soluble salts are removed from the two sulfate plots 6 and 8 than from any of the others.The same is true of the calcium removed, the ammonium sulfate evidently reacting with the calcium in the soil to form calcium sulfate.This is borne out by the increase in the amount of sulfate removed from these two plots.These results are similar to those obtained by Lawes and Gilbert at Rothamstead,in their study of the drainage waters from ammonium-sulfate treated plots in comparison with those differently fertilized.The protective action of sodium nitrate for calcium is again shown,as the amount of calcium removed from the nitrate plot 1 is smaller than that removed from the other plots.The increase in the amount of sodium and potassium chlorides removed from this plot is due to the sodium nitrate.While the above table would lead one to think that the drainage waters from the different plots had a

radically different composition from one another, this is not true, as a study of the average percentage composition of the fixed solids will show.

Table IX.-Average Percentage Composition of
Fixed Solids.
1913.

Plot	Calcium Oxide		Sulfur Trioxide		Chlorine	
	Spring	Fall	Spring	Fall	Spring	Fall
0 ---	28	28	48	47	9	9
1 ---	21	18	40	34	19	22
6 ---	36	31	48	42	15	18
7 ---	33	32	42	32	18	27
8 ---	36	32	47	38	14	11

While the waters differ somewhat in their composition the main difference between them is in the concentration. The waters from the sulfate plots are more concentrated than the others.

The theory that calcium when removed from the soil through fertilization with ammonium sulfate, is removed in the form of calcium sulfate is borne out by the above results. This is more clearly shown by the ratio of calcium oxide to sulfur trioxide, which is fairly constant for the plots.

As the waters from the limed and unlimed parts of the plots cannot be kept separate, the difference due to liming one-half of each plot cannot be determined. To determine if possible whether any difference existed, the following experiment was conducted with soil from the limed and unlimed areas of plots 5 and 6.

Galvanized-iron cylinders 3 inches in diameter were driven into the soil to a depth of eight inches, and a column of soil thus removed. The soil was left in the cylinder just as it was removed and taken to the laboratory. A linen cloth filter was then placed over the bottom of the cylinder and the soil saturated with distilled water. When saturated, 500 cubic centimeters of distilled water were poured on top and allowed to percolate through. This was repeated five times, making six percolates from each sample. Three samples from each plot were treated this way.

For purpose of analysis the second to the sixth percolates, inclusive, were combined into one sample. The solutions were then analyzed for total and fixed solids, calcium, sodium, potassium, magnesium, iron, aluminum, sulfates and chlorides.

Table X.- Composition of Percolates in Parts per 100.000.

	Plot 5 Limed		P.5 Unlimed		Plot 6 Limed		P.6 Unlimed	
	1st.	Combined	1st.	Combined	1st.	Combined	1st.	Combined
Total Solids,	83.10	23.20	79.30	27.50	89.90	24.50	112.30	29.70
Fixed Solids,	67.30	18.60	66.40	23.50	72.20	19.70	97.30	24.00
Calcium oxide,	22.45	5.68	17.43	4.92	23.75	6.65	25.53	6.44
Potassium oxide,	.85	.44	3.16	1.80	1.03	.50	3.57	2.36
Magnesium oxide,	1.78	1.11	1.99	.65	.77	.35	1.13	---
Sulfur trioxide,	41.60	10.53	40.09	13.50	28.71	9.59	30.77	13.82
Chlorine,	1.26	.17	.80	.20	10.38	.49	22.45	2.89

Table XI.-Percentage Composition of Fixed Solids.

	Plot 5 Limed,		P 5 Unlimed,		Plot 6 Limed,		P.6 Unlimed	
	1st.	Combined	1st.	Combined	1st.	Combined	1st.	Combined
Calcium oxide,	33.36	30.54	26.25	20.94	32.89	33.76	26.24	26.83
Potassium oxide,	1.26	2.37	4.76	7.66	1.43	2.53	3.67	9.83
Magnesium oxide,	2.64	5.97	2.99	2.76	1.07	1.78	1.16	- -
Sulfur trioxide,	61.81	56.61	60.38	57.45	39.76	48.68	31.62	57.58
Chlorine,	1.87	.91	1.20	.85	14.38	2.48	23.07	12.04

The first difference noticed on studying Table X.is the larger amount of soluble salts removed in the first percolate than in the subsequent portions.That this difference is largely a matter of concentration is shown by a comparison of the constituents as shown in Table XI.The variations between the two plots are those due to the different fertilizers used.Plot 5 has more sulfates and magnesium and less chlorides removed than plot 6.Since plot 5 received its application of potash as low-grade sulfate and plot 6 as muriate of potash,these differences were to be expected,

The variations between the limed and unlimed ends of the plots are very similar.More calcium and less potash are removed from the limed ends than from the unlimed .Traces of iron and aluminum were found in all of the extracts,but showed no difference between the two plots or between the limed and unlimed areas of the plots.

Comparing the percentage composition of the percolates and the drainage waters,both based on the fixed soils,we find them agreeing very closely.The per cent.of calcium oxide in the drainage water of 1913 for plot 6 is 36 as against 30 found in the percolation waters from this plot,averaging the limed and unlimed. Sulfates in the drainage waters are 48 per cent. and in the percolates 44 per cent,and chlorides in the drainage waters

are 15 per cent.and in the percolates 13 per cent. of the fixed solids.The higher results in the drainage waters are probably due to the fact that more of the drainage comes from the limed ends of the plots than from the unlimed.

Summary.

The results of the experiments show that -

(a) The absorption of ammonia from sulfate of ammonia solutions by the soils studied increases with the increase in the concentration of the ammonium-sulfate solution used.This increase is not strictly proportional to the increase in the concentration of the ammonium-sulfate solutions.The soils from two plots previously fertilized with ammonium sulfate without lime absorb less ammonia than do the others.This shows that the continued use of ammonium sulfate has caused some change in the soil.

(b.) The absorption of dyes by these soils is very similar to the absorption of ammonia.More dye is absorbed from the more concentrated solution than from the lesser concentration.The two unlimed sulfate plots also absorb less than do the others, showing that their absorptive powers have been lessened.

(c.) Ammonium sulfate has a solvent action on the calcium in the soils,and depletes the soil of this element.This is shown by the ammonium-sulfate extracts and also by the drainage water analyses.

(d) Ammonium-sulfate seems to have no solvent action on sodium or potassium in the soil in the presence of sufficient quantities of lime.That it has a slight solvent action on potassium in the absence of lime is shown in the percolation experiment,where more is removed from the unlimed plots than from the limed.This may be more beneficial than harmful,as it will make more potash available for the use of the plants.

(e) More iron and aluminum are removed from the two sulfate plots than from any of the others.

PART II. STUDIES OF WATER EXTRACTS.

As the foregoing investigations show that the most noticeable difference between the plots fertilized with nitrate of soda and those fertilized with sulfate of ammonia was in the amount of soluble iron and aluminum removed, further investigations to study these differences were carried on. In the course of these investigations manganese as well as iron and aluminum was found to be removed as a result of ammonium fertilization.

As far as the author is aware, no previous results of investigations on the presence of soluble iron and aluminum in the soil as a result of fertilizer treatment have been reported. Since these investigations were undertaken, Conners[1] has published results to show that aluminum nitrate might be found in an "acid" soil.

The effect of manganese has been studied for a number of years by numerous investigators. In only three cases has the presence of large quantities of manganese in the soil been thought to account for the infertility of the soil. Elwell[2] found considerable amounts of manganese soluble in water in a soil which failed to produce leguminous plants and Guthrie[3] found .254 per cent Mn_2O_3 in bare patches of a golf green. Wilcox and Kelley[4] have found extraordinarily large quantities of manganese in some Hawaiian soils,--as high as 5.61 per cent Mn_3O_4.

The results of numerous fertilizer experiments with different manganese salts have been rather contradictory. In some cases manganese seemed to increase the growth, while in others it either had a negative or harmful result. In general, however, it has been shown that in small quantities--between 50 and 75 pounds per acre--most of the salts have a stimulating action. Above these amounts a decided toxic effect has generally been produced. The toxic action is usually made manifest by chlorosis of the leaves, due, as some claim, to increased oxidation of the chlorophyl.

In order to determine if ammonium sulfate had a solvent action on manganese in the soil similar to its action on iron and aluminum, soil extracts were made in the usual way using tenth-normal and normal solutions of ammonium sulfate. No manganese was found in any of the extracts from the limed plots and only traces in the unlimed plots 1 and 7 with the tenth-normal solution. With the more concentrated solution, traces were found in all of the extracts from the limed plots. The table shows the amounts found in the extracts from the unlimed plots.

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[1] Ind. Agr. Expt. Sta. Bul. 170.
[2] Science No. 399 (1902) p. 291.
[3] Agr. Gaz. N. S. Wales 21 (1910).
[4] Hawaii Expt. Sta. Bul. 28.

Table.- Mgs of Mn_3O_4 from 100g of Air-dried Soil.

	N/10 $(NH_4)_2SO_4$	N $(NH_4)_2SO_4$
Plot 1 Unlimed	trace	.58
Plot 6 "	.88 mg.	1.52
Plot 7 "	trace	1.18
Plot 8 "	.63 mg.	1.45

The ammonium sulfate removed marked amounts from all of the plots thus showing that it has a solvent action on the manganese in the soil. The larger amounts removed from the two sulfate plots would indicate that they already contained some soluble manganese salts, due to the previous fertilizer treatment.

As was stated in the first part, no iron or aluminum was found in the water extracts of the soils when prepared in the usual way of 5 parts water to one part soil with two hour treatment. In order to determine if an increase in the ratio of water to soil or the length of time of standing in contact would influence the amount of these substances going into solution the following experiment was tried.

Five sets of two hundred grams of air-dried soil from the limed and unlimed ends of plots 1.6.7 & 8 were weighed out and treated as follows:

	Soil, g.	Water, cc.	Treatment.
1.	200	1000	Filtered after 2 hours
2.	200	10,000	" " " "
3.	200	100,000	" " " "
4.	200	1000	" " 7 days
5.	200	10,000	" " 7 days.

All of the extracts were filtered through porcelain filters under pressure and those of more than 1 liter volume were evaporated to one liter. The extracts were analyzed for total solids, iron, aluminum, manganese and silica. Fixed solids were determined by heating the total solids to faint redness and weighing the residue.

Fixed Solids in Milligrams from 100g Air-dried Soil.

	Two hour treatment 1-5	1-10	1-20	One week 1-5	1-10
Plot 1 limed	18	21	27	40	28
Plot 1 unlimed	20	12	24	28	28
Plot 6 limed	17	30	25	43	27
Plot6unlimed	22	32	54	37	27
Plot 7 limed	25	16	29	43	38
Plot 7 unlimed	12	16	119	37	29
Plot 8 limed	23	22	--	42	29
Plot 8 unlimed	18	36	48	37	29

The results are rather contradictory. While an increase in the amount of soluble material is found with an increase in the proportion of water to soil in the two hour treatment, the reverse is true when the longer treatment is used. Iron and aluminum were only found in traces in all of the extracts. Silica was found in small quantities in all of the extracts but showed no differences between the different plots with the exception of the extracts from the unlimed end of plot seven in the 1-20 treatment, where the high fixed solids is due to silica.

Manganese showed the most striking differences as a result of the different treatments. No manganese was found in the 1-5 and 1-10 extracts when in contact two hours. The manganese found in the other extracts is shown in table.

Manganese in mgs of Mn_3O_4 from 100g air-dried Soil

	Two hour treatment 1-20	One week 1-5	1-10
Plot 6 Limed	none	.35	trace
Plot 6 unlimed	.229	1.53	1.23
Plot 7 unlimed	none	.40	trace
Plot 8 unlimed	trace	1.12	.72

The other extracts showed no trace of manganese. As traces of iron and aluminum were found in these extracts it was decided to use larger quantities of soil and see if measurable amounts of these substances could be obtained. For this purpose eight kilograms of air-dried soil from the unlimed ends of plots 1,6 and 8 were placed in glass jars with an opening in the base plugged with glass wool and covered with a linen filter.

Enough distilled water was then added to saturate the soil and then left in this condition two days.Eight liters of water were then percolated through the soil.The water was added in portions of one liter,and a second portion was not added until the first had percolated through.The percolates were all concentrated to one liter on the water bath and ~~then~~ filtered through filter paper,but as the filtrate from plot 6 was still turbid all these extracts were filtered through porcelain filters.Despite the fact that the extracts of plots 1 and 8 appeared perfectly clear before filtering they required three hours to filter with an average pressure of forty pounds while the extract from plot 6 required but one half hour.The slowness with which these filtered would seem to indicate that colloids were present in the extract.

On addition of ammonium hydroxide to the extracts and heating,a heavy flocculent precipitate formed in each one.The precipitate was filtered,washed and dried after which they were analysed and found to have the following compositions.

Compositions of NH_4OH precipitate calculated to millegrams from 100g soil.

	Plot 1 unlimed	Plot 6 unlimed	Plot 8 unlimed.
*Al_2O_3	.059	.106	.087
SiO_2	.161	.457	.500
CaO	1.403	none	none
Mn_3O_4	none	1.30	.318

* trace at Fe_2O_3

The analysis shows that more iron and aluminum and manganese is removed from the two sulfate of ammonia plots than from the nitrate plot.It is of interest to note that in the extract from plot 1 large amounts of calcium were precipitated by the ammonia and seemingly as the carbonate,as there was a marked effervescence when hydrochloric acid was added to the precipitate.

On further heating the filtrate from the above and adding a few drops of ammonium hydroxide a second precipitate formed in all three of the extracts.This precipitate was not due to an insufficient amount of the precipitating agent having been added,as the first filtrate had an excess of ammonia. The method of formation of the precipitate and the fact that part of it redissolved on washing indicate that it was a colloid.

The precipitation took place because the concentration of the solution had reached the limit of stability of the colloid; in other words, the concentration became so great that the tendency for the colloid particles to coalesce overcame the tendency to remain in suspension. The table gives the composition of the precipitates in percentage as well as in milligrams of the different substances removed from 100 grams of soil.

Composition of Second NH_4OH precipitate.

	Plot 1 unlimed		Plot 6 unlimed		Plot 8 unlimed	
Vol. matter	41.87%	-------	15.34%	----	28.50%	----
Al_2O_3	.93	.015 mg	10.51	.046 mg.	2.50	.024 mg
SiO_2	14.19	.220 "	18.35	.081 "	34.25	.335 "
CaO	35.50	.552 "	none	none	23.00	.225 "
Mn_3O_4	none	none	75.85	.296 "	4.50	.044 "

The precipitates are slightly different in composition from the first ammonium precipitates. This is especially true of the precipitate from plot 8 unlimed which contains considerable lime, while in the first precipitate none was found. In the case of plot 1 the amount of lime has fallen off. The precipitate from plot 6 seems to be largely manganese. The calcium in plots 1 and 8 seems to be present as carbonate, there being marked effervescence when hydrochloric acid was added to the precipitate. The precipitate further shows the presence of soluble iron, aluminum and manganese compounds in the soils which have been treated with ammonium sulfate. The above experiments were repeated, using one kilogram samples of soil. The limed ends of the plot were also included. The soil was treated in the same way as in the previous experiment and proportionally smaller amounts of water were used. The extracts were all filtered through porcelain filters.

On the addition of ammonium hydroxide, no precipitate formed in any of the extracts, showing that only small amounts, if any, of aluminum were present. Iron was determined colorimetrically and the following amounts found.

Milligrams of Fe_2O_3 from 100 g. air-dried soil.

	Limed.	Unlimed.
Plot 1	.157	.047
Plot 6	.076	.070
Plot 7	.172	.093
Plot 8	.046	.065

Contrary to expectations the limed ends of the plots in all cases except one gave higher results than the unlimed, and the plots receiving no ammonium sulfate had more present than the sulfate plots.

In determining manganese none was found in any of the extracts from the limed ends of the plots and only a trace in the unlimed portion of plot 1.

Millegrams Mn_3O_4 from 100g soil.

Plot 1	unlimed	trace
Plot 6	"	1.49
Plot 7	"	.49
Plot 8	"	.47

As in the previous experiments the unlimed sulfate of ammonia plot (6) gave the greatest amount.

In a series of experiments conducted in a similar manner with samples of soil collected in the fall of 1915 no iron was found in any of the extracts, and the amount of manganese was considerably less than that found in previous samples. No manganese was found in any of the limed extracts nor in the extracts from the unlimed end of plot 7. The average amounts found from the unlimed sulfate of ammonia plots 6 and 8 were as follows: Plot 6, 2.87 mgs; Plot 8, 1.04 mgs. from 100 grams of soil.

As several of the foregoing experiments had indicated that colloids might be present in the extracts an attempt was made to separate them and determine their composition. The method followed was the one described by Thaer[1]. Eight kilograms of soil from the unlimed end of plot 6 and the limed ends of plots 6 and 8 were extracted with water as in the previous experiments. Owing to the mass of suspended clay which could not be removed by filtering through filter paper, the extracts were filtered through porcelain. While this filtering undoubtedly removed some of the colloids in the extracts, a precipitate of a colloidal nature separated out at the point mentioned by Thaer. The air-dried weights of the different colloids was as follows:

Plot 6	Limed	1.6120g
Plot 6	Unlimed	.2415g
Plot 8	Limed	.1850g

On analyzing the colloids they were found to have the following composition.

Composition of Soil Colloids.

	Plot 6 Limed	Plot 8 Limed	Plot 6 Unlimed.
H_2O and Vol Matter.	31.40%	82.60%	1[illegible].40%
*SiO_2	5.34	25.18	4.49
*SO_3	67.59	48.85	53.59
*CaO	44.38	68.14	34.39

* On non volatile solids basis.

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[1] Jour.f Landw.Vol.60.

Traces of iron were found in all the precipitates. The precipitates had a somewhat different composition from the colloids, the most notable difference being the large amount of silica found. The precipitate from the unlimed sulfate plots had in addition ~~to have~~ some manganese sulfate present.

In order to determine if the conditions of the soil were the same in previous years, samples of soil from the limed portions of plot 6 and the unlimed portions of plots 5 and 6, collected in the fall of 1912 and a sample from the limed end of plot 8 collected in the fall of 1910 were extracted in the same manner as in the previous experiments.

On analyzing the extracts for iron, aluminum, silica and manganese the following results were obtained; No iron or aluminum were found in the extracts from the limed plots. In the extracts from the unlimed plots 5 and 6, 15% Al_2O_3 and .03% Al_2O_3 respectively was found. Silica determinations showed that like amounts in small quantities were present in all the extracts.

Manganese was found in all of the extracts but only in traces in those from the limed plots. The unlimed plots gave the following amounts, figured to 100 grams of air-dried soil.

Plot 5 2.36 mg Mn_3O_4
Plot 6 3.18 mg " "

These results show that the same conditions existed four years ago as are found at the present time.

Having found that the ammonium sulfate in the soils seems to have a solvent action on manganese, iron and aluminum compounds ~~in the soil~~ it was thought desirable to test out other soils that had been similarly treated. This was made possible through the cooperation of Dr. Thorne of the Ohio Experiment Station and Dr. Hartwell of the Rhode Island Station[1] Soils that had previously been fertilized with ammonium sulfate were obtained from both stations.

The Ohio soil is a rather heavy clay loam and was taken from Section C of the five year rotation experiment described in circular 144 of the Ohio Experiment Station page 69. The rotation consists of the following crops grown in the order named; corn, oats, wheat, clover and timothy, the section from which the samples were taken being in clover at the time of sampling, The experiment was begun in 1893 and the unlimed ends of the plots sampled had never been limed. The samples were taken from the limed and unlimed ends of plot 8 and plot 24 which receive the following fertilizers:

Plot 8-80 pounds acid phosphate, 80 lbs. muriate of potash to corn and oats and 100 lbs. acid phosphate and 100 lbs. muriate of potash to wheat.

Plot 24--160 lbs. acid phosphate, 80lbs. muriate of potash, 80 lbs. sulfate of ammonia to corn and oats and 160 lbs. acid phosphate, 100lbs. muriate of potash and 60 lbs. sulfate of ammonia. The clover and timothy were not fertilized.

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[1] Soils from the Pennsylvania Expt Sta. were received too late to be included.

In regard to the growth of clover on Plot 24 Dr.Thorne writes as follows:"For several years there has been practically no clover on the unlimed ammonium sulfate plots in our work. There are occasionally a few scattering plants,but probably not 20 plants on the entire 20th acre plot". Speaking of the limed end of the plots,he states further - "--you cannot distinquish between the three plots(23,24 & 25) although if you were to go through the field you would see that the growth on plot 25 unfertilized is much less luxuriant than on plots 23 & 24;in other words,the clover on this land requires fertilizers as well as lime,and when the ammonium sulfate is neutralized with lime,we get a luxuriant growth.There is also more or less sorrel on this land whenever the clover growth is so weak as to give room to the sorrel.There are usually at the beginning of the season as many clover plants on the unlimed as on the limed land,but they do not get much beyond the nutrient furnished by the seed and by harvest have disappeared."

The soil from the Rhode Island Station is taken from the permanent plots 23,25 and 29 and is a sandy loam type.The plots have received the same fertilizer treatment with only differences in quantity applied since 1893.The fertilizers applied have been as follows:-

Plot 23 - Ammonium sulfate,acid phosphate,muriate of potash.
Plot 25 - " " " " " " "
Plot 29 - Sodium nitrate, " " " " "

The amounts applied the past season on an acre basis were as follows:- In the spring 50 pounds of nitrogen in nitrate of soda or sulfate of ammonia,125 pounds phosphoric acid (P_2O_5) in acid phosphate and 100 pounds potash (K_2O) in low grade sulfate of potash,in July,30 pounds of nitrogen in nitrate of soda or sulfate of ammonia,75 pounds phosphoric acid in acid phosphate and 60 pounds of potash in low grade sulfate of potash were applied.

In addition plots 25 and 29 have been limed in 1893,1894, 1902 and 1915.In 1915 plot 23 was also limed for the first time since the plots were laid out,receiving 500 pounds CaO per acre.Plot 25 received at the same time 1500 pounds per acre and plot 29,1000 pounds per acre of CaO.Plot 23 was limed,Dr.Hartwell states,because it "was becoming so very unsuitable for crop growth----.Under these conditions (i.e.Liming) certain crops made an exceptionally good growth on plot 23."

These soils were treated in exactly the same way as our own soil,being air-dried and passed through a seive having seven holes to the linear inch.Water extractions were made from the Rhode Island soils in the same way as described above,using one kilogram samples.Owing to the nature of the

Ohio soils it was impracticable to obtain percolates in this way, the water percolating too slowly. They were accordingly shaken for two hours on a mechanical shaker with twice as much water as soil and then filtered through filter paper and finally through porcelain filters under pressure. Determinations were then made for iron, aluminum, manganese and acidity.

The extracts from the Ohio soil were neutral to indicators in every case while the extracts from plots 25 and 29 of the Rhode Island soils were slightly alkaline and plot 23 slightly acid, requiring .6 cc N/10 ammonium hydroxide to neutralize it.

Tests for manganese showed that none was present in any of the Rhode Island soils. The Ohio soils showed manganese in all cases. The amounts found being as follows:

Manganese as Mn_3O_4 in mg from 100g soil.

Plot 8 limed	trace
Plot 8 unlimed	.16 mg.
Plot 24 limed	.03 mg.
Plot 24 unlimed	.64 mg.

One notes the same result that was observed previously with the Amherst soils, much more manganese being removed from the unlimed ammonium sulfate plots than from the limed or no nitrogen plots. The iron determinations do not give as concordant results as those with manganese, the amounts of iron found in the different extracts varying rather widely.

Fe as Fe_2O_3 in mg from 100g soil.

Ohio.	
Plot 8 limed	trace
Plot 8 unlimed	.050 mg.
Plot 24 limed	none
Plot 24 unlimed	.031 mg
Rhode Island.	
Plot 23.	.19-.36 mg
Plot 25.	trace
Plot 29.	none.

The results with the Ohio soil are again similar to the results with the Amherst soils, more iron being found in the extracts of the no nitrogen plot than in the extracts from the ammonium sulfate plot. The results with the Rhode Island soil are just the reverse, much more iron being found in the extract from the ammonium sulfate plot than in the extracts from the other two plots.

Aluminum determinations were also made on all of the extracts but none was found in any except Plot 23 of the

of the Rhode Island samples where 3mgs Al_2O_3 from 100g of soil were found. The precipitate also contained some iron.

Summary.

Briefly summarizing the results of the foregoing experiments we find that from soils that have been fertilized with ammonium sulfate without lime appreciable amounts of iron, aluminum and manganese are removed by washing with water, while where lime has been applied with the sulfate of ammonia no iron, aluminum and manganese or only traces have been removed.

PART III. CULTURE STUDIES.

In order to determine to what extent the substances found in the soil extracts, iron aluminum and manganese might influence plant growth culture work of various kinds was undertaken.

The first culture work ~~undertaken~~ was to determine ifthe infertility of the soils extended to their water extracts as was found by Whitney[1], Livingston[2] and others.

The seedlings used were rye, barley and red clover, which were germinated on paraffin covered wire gauze as described in Bulletin No. 40, Bureau of Soils. When the stems of the seedlings reached a length of one inch they were transferred to notched corks and placed in the culture solutions.

The culture solutions were contained in salt-mouthed bottles of 250 cubic centimeters' capacity, with necks having a diameter of 1¼ inches. Four seedlings were placed in each bottle. As each experiment was carried on in triplicate this gave a total of twelve seedlings for each treatment.

The soil extracts were made by mixing two parts water with one part soil and letting the mixture stand for about two hours with frequent shakings, when the water was either poured off or filtered through porcelain filters under pressure.

The first series was conducted with extracts from the limed and unlimed ends of plots 1, 6, 7, and 8. One set was made up with filtered extracts, and a second set with the unfiltered extract. The seedlings used were rye and red clover. The experiment was continued four weeks, at the end of which the plants began to wilt.

The first differences were noted at the end of the first week, the rye seedlings in the extracts from the limed ends of the plots being better than those in the extracts from the unlimed areas. The seedlings in the extracts from the unlimed areas all had a reddish-colored stem, and did not make as good a growth as the others. The clover seedlings showed similar differences, but more in the roots than in the tops. The differences became more marked as time went on, and differences in the root development became noticeable. The roots in the extracts from the unlimed end of plot 6 became stunted and thickened, and the roots in the extract from the unlimed end of plot 8, while not stunted, showed a poorer growth than the others. When the experiment was discontinued the seedlings in the extract from the limed end of the plot 1 and 8 were the best, with the poorest in the extracts from the unlimed ends of plots 6 and 8. As the clover seedlings did not make much growth they were omitted in the second series and only barley was used. Barley was chosen, as it has been found to be more sensitive to toxic substances than rye seedlings. The filtered extracts were also omitted, as no differences were noticeable between the filtered and unfiltered extracts in the first series.

As in the first series the second was continued four weeks. At the end of the first week no differences were noticeable in the tops, but the roots in the extract from the unlimed end of plot 6 again showed the stunted and thickened appearance. At the end of two weeks the tops in the extracts from the unlimed ends of the plots began to wilt, the tips of the leaves turning white.

When the experiment was discontinued the seedlings in the extracts from the limed ends of the plots appeared just about alike while in the extracts from the unlimed ends the poorest were the seedlings in the extract from plot 6. The seedlings were weighed green, but the weights did not show the differences which were apparent to the eye.

A third experiment using red clover seedlings with soil extracts as the nutrient media in which the amount of iron, aluminum and manganese had been determined was started but owing to the unfavorable weather conditions the plants did not make much growth. The same differences were however noticeable and the addition of calcium carbonate did not have any beneficial action, the plants in the soil extract from the ammonium sulfate plots with and without the addition of lime were alike, both being the poorest plants in the series.

Experiments were next undertaken to determine whether ornot iron and aluminum exerted a toxic action on plants and whether calcium carbonate or sulfate would counteract the toxicity.

At the time the culture experiments were undertaken practically no work of this nature, using iron and aluminum salts in culture solutions had been reported. The only experiments known being those at the Rhode Island station[1], Since then however, Connors[2] of Indiana has published results on the toxic action of aluminum on corn seedlings and Gile[3] has published results of the toxic effect of salts of iron on rice seedlings.

The salts used in the following experiments were ferrous sulfate and aluminum ammonium sulfate. The alum was used instead of aluminum sulfate because the latter was not on hand. Standard solutions of these salts of one tenth molecular strength were made up and different amounts added to the nutrient solutions.

The nutrient solution used was slight modifications of Pfeffers and was made as follows:

Solution (a): 20.5g $Mg\ So_4$ dissolved in 350 cc distilled water.

Solution (b): 40g $Ca\ (NO_3)_2$, 10 g KNO_3 20.56g $Na_2\ HPO_4$ dissolved in 250 cc distilled water.

One hundred cubic dentimeters of solution (a) and 100 cubic of solution (b) were then added to 9.8 liters of distilled water and a few drops of ferric chloride solution added. Red clover seedlin were used in All subsequent experiements as the toxic action of the soil in the field was most marked on the clover crop.

The seeds were germinated on perforated paraffin disks covered with cloth netting and floated on water, similar to the paraffin coated wire gauze used in the earlier experiments.

The first experiment was carried on with alum salt only.

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[1] RI Ann. Rpt. 1907 [2] Indiana Expt. Sta. Bul. 170

[3] Jour. Agr. Research Vol. #3

Treatment employed in First Experiment.

1. Nutrient solution (check).
2. Nutrient solution--solution of ammonia alum= 216 parts per million of Al.
3. Nutrient solution--solution of ammonia alum= 108 parts per million Al.
4. Nutrient solution--solution of ammonia alum= 43 parts per million Al.
5. Same as No. 2--CaO
6. Same as No. 3--CaO approximately .5 gram of CaO was added
7. Same as No. 4--CaO to each bottle.

At the end of the first week quite marked differences were noticed in the roots, while the tops of all but the check were about alike. The roots of all but the check and No. 7 (43 p.p.m. Al --CaO) were very much stunted. The roots consisted of the single taproot without root hairs. Four days later the tops began showing differences similar to the roots. The worst seedlings were those in the highest concentration of aluminum, the conditions improving with a decrease in the amount of aluminum present. The presence of the calcium oxide seemed to counteract the toxic effect in a marked degree but not entirely, except in the most dilute solution. At the end of four weeks when the experiment was discontinued, the differences were the same as noted at the end of the first week, only more pronounced. The seedlings in the bottles containing 216 parts per million (No 2) and 108 parts per million (3) of the aluminum, respectively, had died at the end of the third week, even in those treated with calcium oxide. The check was in excellent condition and No. 7 (43p.p.m. plus CaO) was fair.

In the second experiment a series of cultures with ferrous sulfate was added and instead of using calcium oxide to neutralize the toxic action of the aluminum salt the carbonate and sulfate were used in order to avoid the danger of having the nutrient solution become alkaline from the calcium oxide. Enough of the carbonate and sulfate was added to make a saturated solution.

Treatment employed in Second Experiment.

1. Nutrient solution
2. Nutrient solution--$CaCO_3$ } Checks.
3. Nutrient solution--$CaSO_4$ }
4. Nutrient solution--aluminum sol.= 43 p.p.m. of Al.
5. Nutrient solution--Al sol.--$CaCO_3$
6. Nutrient solution--Al sol.--$CaSO_4$
7. Nutrient solution--Al.sol.=21.6 p.p.m. of Al.
8. Nutrient solution--Al sol.--$CaCO_3$
9. Nutrient solution--Al sol. --$CaSO_4$

10. Nutrient solution--$FeSO_4$ sol. 220 p.p.m. of Fe.
11. Nutrient solution--$FeSO_4$ sol.--$CaCO_3$
12. Nutrient solution--$FeSO_4$ sol--$CaSO_4$
13. Nutrient solution--$FeSO_4$ sol= 110 p.p.m. of FE.
14. Nutrient solution--$FeSO_4$ sol.--$CaCO_3$
15. Nutrient solution--$FeSO_4$ sol.--$CaSO_4$
16. Nutrient solution--$FeSO_4$ sol.=45 p.p.m. of Fe.
17. Nutrient solution--$FeSO_4$ sol. --$CaCO_3$
18. Nutrient solution--$FeSO_4$ sol. --$CaSO_4$

At the end of three days most of the plants in the higher concentrations of the ferrous sulfate had died. These were replaced, but by the end of the first week these too had died. This failure of the plants to make a start was, I think, in part due to unfavorable weather, there being practically ~~in the first experiment~~ no sunshine during this first week, The same differences as indicated in the first experiment were noticed in this series. Calcium carbonate counteracted the toxic influence of the aluminum salt in both concentractions to a marked degree, but not entirely. In the iron-treated solutions the calcium carbonate had a slightly beneficial effect on No. 14 (110 p.p.m. of Fe), more beneficial on No. 17 (45 p.p.m/ of FE), but no effect on the highest concentration (220 p.p.m. of Fe). Calcium sulfate had no effect, the plants being similar to those in the solutions of the same concentrations without the calcium salt. It was also noticed that the seedlings in the solutions containing the iron and aluminum salts without the addition of the calcium had a tendency to have stems of a reddish color. The experiment was discontinued at the end of the third week, as most of the plants had died from excessive heat. An extremely hot spell made it impossible to keep the greenhouse cool.

The third experiment was a repetition of the second, with the exception that the highest concentration of ferrous salt was omitted, and a more dilute one added.

Treatment employed in Third Experiment.

1. Nutrient solution
2. Nutrient solution --$CaCO_3$/Checks
3. Nutrient solution --$CaSO_4$
4. Nutrient solution--aluminum sol.=43 p.p.m. of Al.
5. Nutrient solution--aluminum sol.--$CaCO_3$
6. Nutrient solution--aluminum sol.--$CaSO_4$
7. Nutrient solution--aluminum sol.==21.6 p.p.m. of Al.
8. Nutrient solution--aluminum sol.--$CaSO_3$
9. Nutrient solution--aluminum sol.--$CaSO_4$
10. Nutrient solution$FeSO_4$ sol.=110 p.p.m. of Fe
11. Nutrient solution-$FeSO_4$ sol.--$CaCO_3$

12. Nutrient solution--$FeSO_4$ sol.--$CaSo_4$
13. Nutrient solution--$FeSo_4$ sol.= 44 p.p.m/ of Fe.
14. Nutrient solution--$FeSo_4$ sol.--$CaCO_3$
15. Nutrient solution--$FeSO_4$ sol.--$CaSO_4$
16. Nutrient solution--$FeSo_4$ sol.= 22 p.p.m. of Fe.
17. Nutrient solution--$FeSO_4$ sol.--$CaCO_3$
18. Nutrient solution--$FeSO_4$ sol.--$CaSO_4$

As in the previous experiments the roots showed marked differneces at the end of the fourth day, while the tops showed no differences until a week had elapsed. The roots of the aluminum and iron treated bottles were very much stunted, and either consisted of only one main taproot without laterals or root hairs, or else quite a number of short thick roots growing from the base of the stem. The laterals only grew about a sixteenth of an inch and then stopped. All the stunted roots were thicker than the unaffected ones, and despite their much smaller number and shorter length weighed as much as the healthy roots. At the end of six weeks the experiment was discontinued. The seedlings in the 22 parts per million iron solution No. 16 were almost normal, and where calcium carbonate had been added (No. 17) showed practically no differences from the check. The seedlings in the 44 parts per million iron solution (No. 13) made little growth after the first week, but did not die, and where calcium carbonate was added the toxic action was in part overcome. In the 110 parts per million iron solution (No. 10) the plants died at the end of the fourth week. Calcium carbonate in this case seemingly had no effect. As was already noted in the second experiment calcium sulfate had no effect in counteracting the toxic action of the salts. The results with the aluminum salt were exactly similar tothose of the first and second experiment.

Summarizing the results of the experiments with iron and aluminum salts we find as follows:

1--That aluminum sulfate when present in culture solutions in concentrations greater than 40 parts per million of aluminum has a very toxic action on clover seedlings.

2--That ferrous sulfate when present in culture solutions in concentrations above 40 parts per million of iron exerts a toxic effect on clover seedlings.

3--That this toxic action of iron and aluminum can in a large measure be overcome by the use of calcium carbonate up to a certain point, beyond which it has no effect. Calcium sulfate does not have this beneficial

effect.This difference in the action of the two calcium salts is due to the fact that the carbonate precipitates the iron and aluminum as the hydrated oxide thus removing them from solution and conteracting their harmful action.The toxic action of the higher concentrations of iron and aluminum,despite the excess of calcium carbonate present can be explained I beleive as follows:When the calcium carbonate reacts with the ferrous sulfate,calcium sulfate is formed.As the calcium sulfate is quite soluble it goes into solution until the solution becomes saturated.The presence of the large number of Ca ions will then force back the solubility of the Calcium carbonate and thus prevent its reacting with the remainder of the ferrous sulfate. The reaction with the aluminum salt is analogous.

4. The theory that the toxicity of iron and aluminum is due to the penetration of the salts into the seedlings does not seem to be borne out as a microscopical examination of the roots showed that the outer layer of cells was plasmolyzed,thus arresting the development of the roots.That the poisoning did not extend to the whole roots is further shown by the large number of short roots which developed from the root above the solution but were arrested in their development as soon as they entered the solution.As a third point,the continued growth of the tops for a week after the stunted appearance has made itself manifest on the roots,indicates that the injury is confined to the roots.The plants finally die,I beleive because of a lack of nourishment rather than to a poisoning of the entire seedling.

To determine the toxicity of manganese to clover seedling the following experiments were undertaken.The same nutrient solutio as was used in the previous experiment was employed.The manganese salt used was the sulfate $Mn\ SO_4.4H_2O$.

The treatment in the first experiment was as follows.

No.1 Nutrient solution.
No.2 " " $Ca\ CO_3$
No.3 " " $Ca\ SO_4$
No.4 " " $Mn\ SO_4$ = 40 ppm of Mn
No.5 " " $Mn\ SO_4 + Ca\ CO_3$
No.6 " " $Mn\ SO_4 + Ca\ SO_4$
No.7 " " $Mn\ SO_4$ = 100 ppm of Mn
No.8 " " $Mn\ SO_4 + Ca\ CO_3$
No.9 " " $Mn\ SO_4 + Ca\ SO_4$
No.10 " " $Mn\ SO_4$ = 200 ppm of Mn
No.11 " " $Mn\ SO_4 + Ca\ CO_3$
No.12 " " $Mn\ SO_4 + Ca\ SO_4$
No.13 " " $Mn\ SO_4$ = 300 ppm of Mn
No.14 " " $Mn\ SO_4 + Ca\ CO_3$
No.15 " " $Mn\ SO_4 + Ca\ SO_4$

The experiment was conducted outdoors in the pot yard in place of in the greenhouse used in previous experiment, the seedlings being put under cover at night and during inclemen weather.The experiment was continued four weeks.

The effect of the manganese was noticed after the first week.Those with manganese did not grow as fast as the checks and also began to show chlorsis of the leaves.The roots did not have a stunted appearance as was noticed when iron and aluminum salts were used,but seemed to be simply underdeveloped.Neither the presence of calcium carbonate nor sulfate had any beneficial effect.In some cases the calcium carbonate seemed to aggravate the toxicity rather than alloviate it.When the experiment was discontinued the tops in the most concentrated manganese solutions had died and those in the most dilute had apparently lost all their chlorophyl.

The tops and roots of the plants were dried and

manganese determinations made on them. The table shows the amounts of Mn_3O_4 found in 1 gram of oven-dried samples.

Manganese as Mn_3O_4 in clover plants.

	Tops. mgs.	Roots. mgs.
Check	none	none
40 ppm Mn	2.01	17.94
100 ppm Mn	4.56	58.80
200 ppm Mn	5.02	83.90
300 ppm Mn	4.41	75.31

The results show that manganese is taken up by the plants in considerable amounts and is carried into the tops. Concentrations above 100 ppm of manganese have little effect in increasing the amount taken up by the plant. While some manganese is carried into the tops, most of it remains in the roots.

In order to determine whether calcium carbonate or sulfate had any beneficial action in more dilute solutions of manganese, a second experiment was undertaken. Masoni[1], Pugliese[2], and Aso[3] have found th t iron salts seem to counteract the toxicity of manganese. In order to confirm their conclusions, one series of experiments was undertaken using a combination of these two salts, another series using manganese plus aluminum salt and still another series using iron and aluminum together.

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1. Staz. Sper. Agr. Ital. 44 (1911) p. 85 Abs. E.S.R. 26
2. Atti R Ist Incoragg. Napoli 6 ser. 65 (1913) p. 289. Abs. Chem. Abs. 9 p. 641.
3. Bul. Agr. College Tokyo V p. 177.

Treatment in second experiment:

No.1 Nutrient solution (check)
No.2 " " + $Mn\ SO_4$ = 20 ppm of Mn
No.3 " " + " + $Ca\ CO_3$
No.4 " " + " + $Ca\ SO_4$
No.5 " " + " = 10 ppm of Mn
No.6 " " + " + $Ca\ CO_3$
No.7 " " + " + $Ca\ SO_4$
No.8 " " + " = 20 ppm + Al sol= 43 ppm Al
No.9 " " + " " + " + $Ca\ CO_3$
No.10 " " + " " + " = 21.6 ppm Al
No.11 " " + " " + " + $Ca\ CO_3$
No.12 " " + " " + Fe sol= 44 ppm Fe
No.13 " " + " " + " + $Ca\ CO_3$
No.14 " " + " " + " = 22 ppm Fe
No.15 " " + " " + " + $Ca\ CO_3$
No.16 " " + Al"sol 43 ppm + Fe sol = 44 ppm
No.17 " " + " " + " + $Ca\ CO_3$

Owing to poor weather conditions the seedlings did not start well and large numbers of them had to be replaced. At the end of the first week differences were noticed; the roots of the manganese plus aluminum solution 43 ppm (No.8) having a stunted appearance. At the end of two weeks both the roots and the tops of No.8 had a stunted appearance. The roots of No.9 (Mn-Al 43 ppm -$CaCO_3$), No.10 (Mn -22 ppm Al), No.11 (same as 10 - $CaCO_3$) and No.16 (Al 43ppm - Fe 44ppm) were also stunted. No.3 (Mn 20 ppm-$CaCO_3$) and No.4 (Mn 20ppm - $CaSO_4$) were poor but not stunted. All of the bottles having iron in solution had a darker color than any of the others. At the end of three weeks the manganese treated seedlings showed evidence of chlorsis, all of the leaves beginning to have a light green or yellowish color. At the end of five weeks

when the experiment was discontinued the best plants were No. 15 (Mn 20 ppm - 22 ppm Fe - $CaCO_3$) with the checks second best. The use of the more dilute manganese still had a toxic action on the seedlings but not so marked as the higher concentrations, the effect not being noticed until the third week. Neither calcium carbonate nor sulfate had any beneficial effect but as was noted in the first experiment if seemed to increase the toxicity to a slight extent. The combination of manganese and aluminum was very toxic and calcium carbonate had only a slight effect in counteracting the toxicity. The roots were almost normal, showing that the characteristic effect of the aluminum --the stunting of the roots--had been partly overcome. The mixture of iron and manganese in the higher concentrations was just as toxic as either one of the two alone. Where calcium carbonate had been added the plants had a normal appearance and were as good as the checks. In the more dilute iron solution which in itself is not toxic, the toxicity of the manganese was largely overcome and where calcium carbonate had been added, the toxicity had been entirely overcome and the plants were better than the checks.

A third series similar to the first of the manganese series was started in order to more definitely prove that calcium carbonate had no beneficial action in counteracting the toxicity of manganese.

Treatment in third experiment.

No.	1	Nutrient	solution					checks.
"	2	"	"	+ $CaCO_3$				
"	3	"	"	+ 10	ppm	Mn		
"	4	"	"	+ 10	"	"	+ $CaCO_3$	
"	5	"	"	+ 20	"	"		
"	6	"	"	+ 20	"	"	+ $CaCO_3$	
"	7	"	"	+ 30	"	"		
"	8	"	"	+ 30	"	"	+ $CaCO_3$	
"	9	"	"	+ 40	"	"		
"	10	"	"	+ 40	"	"	+ $CaCO_3$	

This experiment wasconducted during the winter in the greenhouse and owing to continued cloudy weather the plants did not grow as well as in the previous experiments. The experiment was continued four weeks and at the end of that time showed the same differences noted in the earlier work,

namely chlorosis of the leaves and more pronounced toxicity where calcium carbonate has been added. This increased toxicity with calcium carbonate is contradictory to the results reported by McCool[1], he having found that calcium chloride would counteract the toxicity of manganese to a marked extent. This may be due to the difference in the solutions and seedlings used, as he used manganese chloride, calcium chloride and canada field pea.

Having found that manganese is carried up into the tops of the plants the following experiments were tried to determine if there was an increase in the amount of manganese in the tops of clover grown on plots where the poor vegetation was thought to be due to manganese.

The first crop of clover analyzed was the same as that used by Morse and reported in Bulletin 161. The tops only were analyzed.

Mn in mg Mn_3O_4 in 1g of moisture free clover tops.

	N Fertilizer	Limed	Unlimed
Plot 1.	$NaNO_3$	trace	.076 mg.
Plot 5.	$(NH_4) SO_4$	.054 mg.	.193 "
Plot 6.	$(NH_4) SO_4$	.054 "	.193 "
Plot 7.	none	.031 "	.114 "
Plot 8.	$(NH_4) SO_4$	trace	.171 "

The composition of the clover from the limed portions of the several plots varied very little.

manganese is evidently present in all clover as the plants from the limed portions were all normal healthy looking plants. The plants from the unlimed portions show a marked increase in those plots receiving sulfate of ammonia.

In the spring of 1915 samples of clover tops and grass and clover roots and grass roots were taken from the limed and unlimed portions of plot 5[2]. From the unlimed end two samples were taken, one of normal looking plants and another of poor plants. The plants were brought into the laboratory and the roots carefully washed free of soil, especial care being taken not to break too many of the finer roots. The tops were then cut from the roots and the clover separated from the grass, the same being done with the roots. They were then dried at 75 degrees and ground. The tops were then analyzed for iron, manganese and silica. The roots were only analyzed for manganese as it is almost impossible to wash them entirely free from soil which would invalidate the results for iron and silica.

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[1] Cornell Agr. Expt. Station Memoir # 2 (1913).

[2] Plot 5 is fertilized as follows: $(NH_4)_2 SO_4$, diss bone black, low grade sulfate of potash.

Composition of Clover and Grass Tops and Roots, in mg per 1g oven dry sample.

	Fe_2O_3	Mn_3O_4	SiO_2
Plot 5. Limed clover tops	.63 mg	faint trace	1.72 mg
Plot 5. " grass	-	.053 mg	19.25 "
Plot 5. Unlimed good clover	1.14 "	trace	4.82 "
Plot 5. " " grass	1.91 "	.158 mg	26.64 "
Plot 5. " poor clover	1.34 "	.096 "	5.36 "
Plot 5. " " grass	2.97 "	.272 "	57.35 "
Plot 5. Limed clover roots	-	trace	-
Plot 5. " grass roots	-	.138	-
Plot 5. Unlimed good clover roots	-	.091	-
Plot 5. " " grass "	-	.218	-
Plot 5. " poor clover & grass roots	-	.245	-

A study of the table shows that the manganese is taken up to a greater extent by the poor plants, both clover and grass than by the good plants. The grass seems to be more tolerant than the clover much more being taken up than by the clover. The results would also seem to indicate that the manganese was not evenly distributed throughout the plot but was more concentrated in spots. As it was rather difficult to find normal clover on the plot it might be said that the better spots were the places of smaller amounts of manganese. A somewhat similar condition has been found by Guthrie and Cohen[1] on a golf green.

The variations in the iron content of the good and poor plants are so small as to come within the limit of experimental error. The increased amount of silica in the poor plants is probably due to their more mature state.

As the foregoing experiments with manganese salts in nutrient solutions had shown that calcium carbonate did not counteract the toxicity of the manganese, while in the field, an application of lime to soil, supposedly infertile because of the presence of manganese salts, corrected the toxicity, Pot cultures were started to determine whether calcium carbonate in the soil could counteract the toxicity of manganese.

The soil used was from the unlimed end of plot 7 and the unlimed end of plot 6. As the soil from the unlimed end of plot 6 already contained a large amount of soluble manganese it was first extracted by shaking it for two hours on a mechanical shaker with a volume of water twice that of the soil. The soil was then air dried and passed through the large sieve (7 holes to the linear inch).

Earthenware pots, six inches in diameter and five inches deep were used. Each pot was filled with two kilos of the

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[1] Loc. cit.

air-dried soil.The lime was applied to the surface and thoroughly worked in.The manganese sulfate was applied in solution.The soil was kept at a 25 per cent moisture content. The clover seed was first soaked for eight hours in a solution of calcium hypochlorite and then seeded on the surface of the soil and pressed into contact with it.The soil was then covered with a half inch layer of washed quartz sand to act as a mulch. The treatment employed is shown in the table,there being two pots in each treatment.

Treatment of Pot Cultures.

No.	Soil.	Treatment.
1.	Plot 6 Unlimed	none
2.	Plot 6 Unlimed	$CaCO_3$ 2T per A
3.	Plot 6 Unlimed	Extracted
4.	Plot 6 Unlimed	" + $CaCO_3$ 2T per A
5.	Plot 6 Unlimed	" + $MnSO_4$ 80 pounds per A
6.	Plot 6 Unlimed	" + " " " " " +$CaCO_3$ 2T per A
7.	Plot 7 Unlimed	none
8.	Plot 7 Unlimed	$CaCO_3$ 2T per A
9.	Plot 7 Unlimed	$MnSO_4$ 80 pounds per A
10.	Plot 7 Unlimed	" " " " " +$CaCO_3$ 2T per A
11.	Plot 7 Unlimed	" 100 pounds per A
12.	Plot 7 Unlimed	" " " " " +$CaCO_3$ 2T per A
13.	Plot 7 Unlimed	" 150 pounds per A
14.	Plot 7 Unlimed	" " " " " +$CaCO_3$ 2T per A.

The seed was planted on March 7th and 8th and began to show above the sand on the 9th and most of them had sprouted by the 15th when all the pots were watered for the first time. The plants came up rather unevenly and some replanting was necessary.The replanting was done with seedlings sprouted on parrafin plates.On April 3rd all the pots were thined to 25 plants.The poorest pots at this time were numbers 3 and 5,the extracted soil with and without the addition of manganese.All of the pots treated with manganese sulfate without lime were poorer than those receiving lime.On April 24th the above differences were even more striking.The plants on number 5 having

practically all died, on number 6 where Calcium carbonate had been added in addition, they made a small growth. All of the plants on the extracted soil were poorer than those on the other pots. The extraction had probably removed most of the soluble nutrients.

While no weights can as yet be given to show the relative differences, the experiment already clearly shows that in the field, lime will correct the toxicity produced by manganese salts.

The culture work with manganese salts shows that manganese is very toxic to clovers and that in nutrient solutions calcium carbonate does not counteract the toxicity, but that in the soil the addition of calcium carbonate does counteract the toxicity to a large extent.

The analysis of clovers shows that the manganese is carried up into the tops and that poor clover grown on soil containing soluble manganese salts, contained more manganese than normal clover.

Summary and Conclusion.

That the infertility of soils fertilized continuously with ammonium sulfate without lime is not due to an accumulation of sulfuric acid or to the formation of "humic acids" has been shown by the following:

1.In all of the experiments we find a marked removal of sulfates from these sulfate plots.This might be considered as proof that there had been an accumulation of sulfuric acid,but the studies with sulfate ammonia solutions where we find as many sulfates removed as were added would tend to show that there was no accumulation.

2.The neutral extracts obtained in all cases except plot 23 of Rhode Island soils shows that no soluble acid was present.The acidity of the Rhode Island soil can be explained by the presence of iron and aluminum salts in the solution.

3.The absorption of calcium again proves the absence of any acid or acids in these soils as both the limed and unlimed areas of the sulfate plots absorbed the same amounts. If an acid were present more calcium would be absorbed by the unlimed areas.The foregoing experiments show that in the absence of lime the ammonium sulfate seems to have a solvent action on iron,aluminum and manganese compounds in the soil.The comparatively large differences between the amounts of iron and aluminum removed by the various treatments from the same plot can be explained by the ease with which iron salts hydrolyze.The hydrated oxides formed as a result of the hydrolysis are then held by the soil.The aluminum salts may act in the same way and furthermore the lack of accurate methods for determining small amounts of aluminum make it impossible to accurately determine the amounts removed from the soils.As is indicated by the analysis of ammonium hydrate precipitates from large amounts of soil, it seems that more aluminum is removed than iron.

The reason no iron or aluminum was found in the extracts from the Amherst soils sampled in the fall of 1915 can be accounted for by the unusually wet summer which caused drainage to take place even in mid-summer and this washed out the soluble iron and aluminum as well as some of the manganese.

The manganese determinations show the most concordant results.More manganese is removed from all of the sulfate plots than from any of the others.The one exception in the case of the Rhode Island soils can be explained by the difference in total manganese in these soils.While the Amherst soils have a total manganese content of .083 % Mn_3O_4 and the Ohio soils .098 % the Rhode Island soils only contain .034 % Mn_3O_4.

That iron,aluminum and manganese are very toxic to clovers in nutrient solutions is shown in part II.It is further shown that lime in the form of the carbonate

will counteract or correct the toxicity of iron and aluminum in water cultures and the toxicity of manganese in soil cultures. Clovers grown on the sulfate plots in which large amounts of soluble manganese was found are shown to contain more manganese than normal clover plants.

Whether or not the infertility of the sulfate plots is due to the direct toxic action of the iron, aluminum and manganese salts on the clover plants or whether the action is indirect, the presence of these salts affecting the bacterial flora, still remains to be shown. That the toxicity in either case is not due to the acid radicle of the soluble iron, aluminum and manganese as has been claimed by some writers is I believe shown by the investigations of Heald[1] and of Kahlenburg and True,[2] who showed that in all cases the toxicity of the salts used was due to the basic ion.

The experiments of Conners recently published showing that acid phosphate seems to benefit an acid soil is further proof that the "acidity" or toxicity of the acid soils is due to iron, aluminum and manganese salts. The acid phosphate forms insoluble ferric or aluminum phosphate thus removing these from solution and correcting the "acidity".

The true reason why ammonium sulfate causes infertility seems therefore to be due to the formation of soluble iron, aluminum and manganese salts. When calcium is present in sufficient amounts none of those toxic salts go into solution. The toxicity of an acid soil is not of necessity due to the presence of all three of these salts but may be due to any one of them. That this effect is not a local one applying only to our own soils is shown by the analysis of the Ohio and Rhode Island soils which showed the same effects.

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1. Bot. Gaz. 22 (1896).
2. Bot. Gaz. 22 (1896)..

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